Synthesis and Reactions of Polymers with Photoactive Terminal Groups. 1. Kinetics and Mechanisms of Radical and Anionic Coupling of *N*-Acetyldibenz[*b,f*]azepine Units to Polymer Molecules

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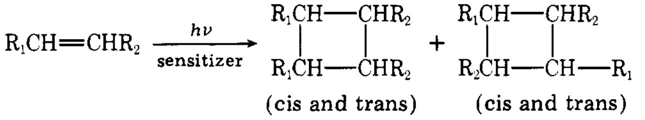
ABSTRACT: The usefulness of *N*-acetyldibenz[*b,f*]azepine groupings in promoting photochemically induced linking of polymer molecules is further demonstrated by chain extension studies of poly(methyl methacrylates) and polystyrenes having terminal dibenzazepine substituents. Chain extension in these materials arises through benzophenone- and benzil-sensitized photocyclodimerization of the central ethylenic double bond of the dibenzazepine moieties. Appropriately functionalized polymers were prepared by (i) photoinitiated free-radical polymerization of methyl methacrylate and styrene employing manganese carbonyl/*N*-bromoacetyldibenz[*b,f*]azepine (BADBA) as initiating components, and (ii) by allowing living double-ended polystyryl anions to react with BADBA. Detailed kinetic and molecular weight studies of the free radically initiated systems substantiate reaction mechanisms previously proposed for manganese carbonyl/organic halide photoinitiating systems and clearly demonstrate the great convenience and applicability of this type of initiation for the synthesis of polymers with specifically functionalized end groups.

Photochemically induced cyclodimerization[1] of ethylenically unsaturated molecules is a well-known process which finds application in photoresist technology.[2] The reaction may be represented generally as in eq 1 and commercially important examples utilize polymers having pendant or main-chain unsaturation of the cinnamate (ArCH=CHCOOR) or chalcone (ArCH=CHCOR) types.

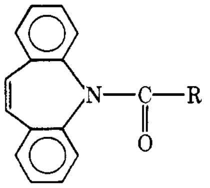


$$R_1CH{=}CHR_2 \xrightarrow[\text{sensitizer}]{h\nu} \begin{matrix} R_1CH{-}CHR_2 \\ |\qquad\ | \\ R_1CH{-}CHR_2 \end{matrix} + \begin{matrix} R_1CH{-}CHR_2 \\ |\qquad\ | \\ R_2CH{-}CH{-}R_1 \end{matrix}$$

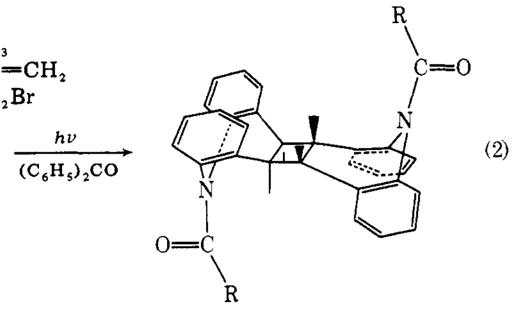
(cis and trans) (cis and trans)

(1)

Recently it was shown[3] that *N*-acyl derivatives of the dibenz[*b,f*]azepine (iminostilbene) ring system (1) may be photochemically cyclodimerized (eq 2) with the aid of a variety of sensitizers having triplet state energies ranging from benzophenone (69.5 kcal/mol) to benzil (53.7 kcal/mol). A range of derivatives (e.g., **1b**) may readily be synthesized which are capable of homopolymerization or copolymerization to products which are photocross-linkable via the dibenzazepine substituents.[4]



1a, R = CH_3
b, R = $CH{=}CH_2$
c, R = CH_2Br



(2)

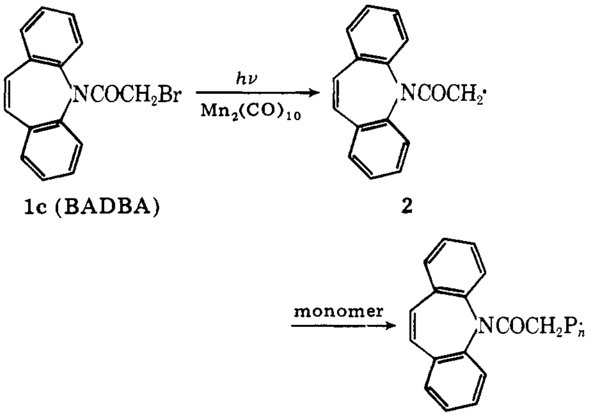
Attachment of structurally related dibenzazepine derivatives to polymer chains as terminal units would afford a convenient procedure for chain extension or block polymer formation by similar photoinduced cyclodimerizations. Such incorporation of specific groups at the ends of polymer chains may be readily accomplished by utilizing appropriately substituted initiator molecules, especially in the case of free-radical polymerizations in which transfer processes may be minimized. Photosensitization by metal carbonyls, of which there are numerous examples, provides a convenient initiation process for such purposes. Many initiating systems of this type include a reactive organic halide (RX) which undergoes a redox reaction with species resulting from photoexcitation of the metal carbonyl to yield a radical (R·) and a halide anion which becomes associated with the oxidized form of the metal as a ligand (eq 3).[5]

$$RX + \text{metal}^0 \xrightarrow{h\nu} R\cdot + \text{metal}^{\text{I}}X \qquad (3)$$

Manganese carbonyl ($Mn_2(CO)_{10}$) is particularly convenient to use as a component of initiating systems and the mechanisms of its photoinduced reactions with organic halogen compounds have been extensively studied.[5–8] Some features of the mechanism of photoinitiation by manganese carbonyl are considered in the discussion section; in conformity with earlier work[5–8] the photochemical process in methyl methacrylate (M) appears to involve unsymmetrical dissociation into two different metal carbonyl fragments (eq 4), of which one subsequently reacts thermally with the organic halide to produce radicals.

$$Mn_2(CO)_{10} \xrightarrow[M]{h\nu} M\cdot\cdot\cdot Mn(CO)_4 + Mn(CO)_6 \qquad (4)$$

N-Bromoacetyldibenz[*b,f*]azepine [**1c**], henceforth referred to as BADBA, is an organic halogen compound which reacts in the usual metal carbonyl photoinitiation systems to yield initiating radicals (**2**); the resulting polymeric product carries the photochemically active *N*-acyldibenzazepine moiety attached to the ends of polymer chains (eq 5).



1c (BADBA) 2

(5)

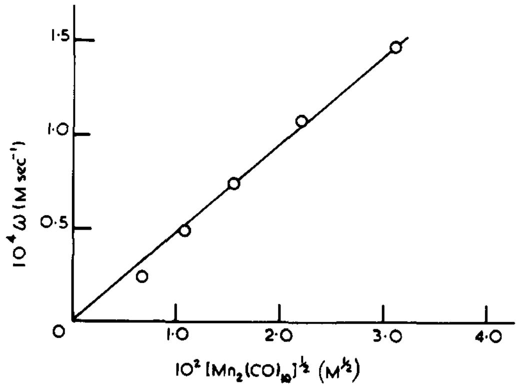


Figure 1. Polymerization of bulk methyl methacrylate at 25 °C photoinitiated (λ 435.8 nm) by $Mn_2(CO)_{10}$ + BADBA. [BADBA] = 0.10 M; reaction time 15 min; intensity constant but arbitrary. Dependence of mean rate ω on $[Mn_2(CO)_{10}]^{1/2}$.

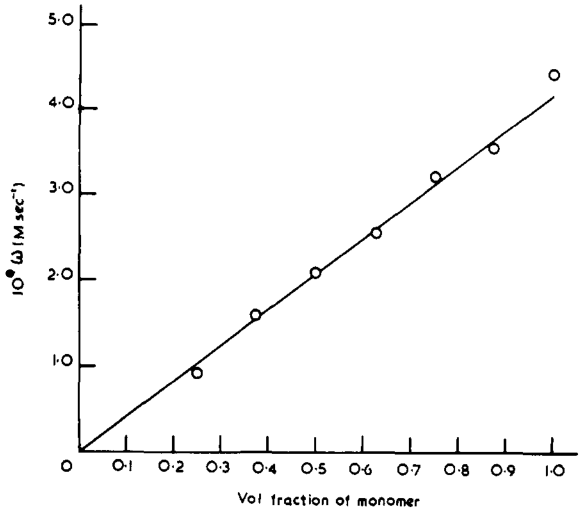


Figure 2. Polymerization of bulk methyl methacrylate at 25 °C photoinitiated (λ 435.8 nm) by $Mn_2(CO)_{10}$ + BADBA. $[Mn_2(CO)_{10}]$ = 3.21×10^{-4}M; [BADBA] = 0.05 M; reaction time 15 min; intensity constant but arbitrary, diluent benzene. Dependence of mean rate ω on volumn fraction of monomer.

The present paper presents results which support the initiation mechanism proposed and demonstrate the feasibility and scope of chain extension via terminal dibenzazepine units.

Experimental Section

Materials. Methyl methacrylate was purified by washing with 10% (w/v) aqueous sodium hydroxide and water to remove stabilizer, drying over anhydrous calcium chloride, and fractionation in vacuum, with retention of the middle fraction. It was then partially polymerized by heating at 85 °C for 3 h and the residual monomer was twice distilled under vacuum. Manganese carbonyl and styrene were purified as described in earlier publications.[6,7]

Benzene and methanol (Analytical Reagent grade) were used without further purification. Tetrahydrofuran and methylene chloride were distilled from calcium hydride while benzophenone and benzil were recrystallized from methanol before use.

N-Bromoacetyldibenz[*b,f*]azepine was obtained from the reaction of dibenzazepine (iminostilbene) (8 g) with bromoacetyl bromide (8.5 g) in benzene (100 mL). The mixture was maintained at reflux for 5 h and evaporated to dryness at reduced pressure with the temperature maintained below 40 °C. The residual solid was dissolved in the minimum volume of benzene and purified by column chromatography on neutral alumina with elution by benzene–hexane (1:2). Recrystallization from benzene–petroleum ether yielded colorless crystals (9.5 g, 72%), mp 138–139 °C. IR and NMR spectra of this material were very similar to those of the corresponding chloroacetyl derivative.[3]

Apparatus and Techniques. Photoinitiated Free-Radical Polymerization. All experiments were carried out in a laboratory illuminated by inactive (sodium) light.

Reactions were initiated by light of wavelength 435.8 nm, the optical system being essentially the same as described in an earlier paper.[7]

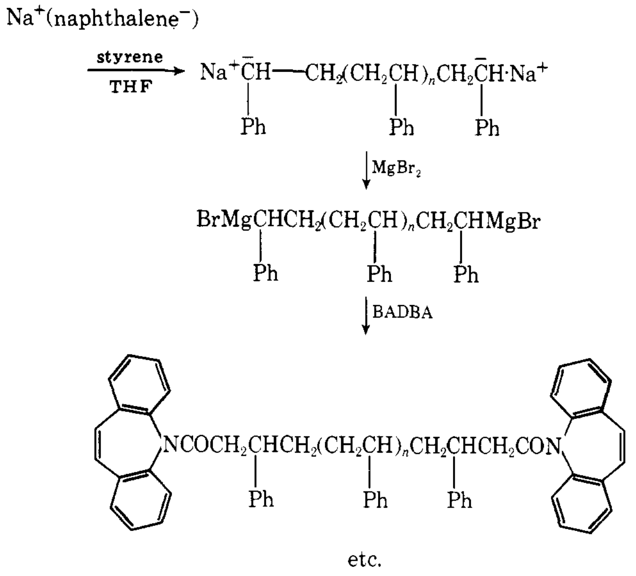
The polymerization was studied gravimetrically at 25 °C in Pyrex reaction vessels (external and internal diameters 13 and 10 mm, respectively). For determinations of the optical density of the reaction mixture with time, reaction vessels were constructed with a side tube communicating with a 10-mm silica optical cell.

Reaction vessels were washed with chromic acid and water and then dried and flamed. Manganese carbonyl and BADBA were weighed directly into the vessels which were then roughly evacuated for 10 s; after introduction of monomer and solvents by distillation on the vacuum line the mixture was thoroughly degassed by the conventional freeze–thaw technique.

When the vessels had been sealed they were irradiated in a thermostat at 25 ± 0.1 °C. Polymers were generally precipitated into methanol, filtered off, dried, and weighed.

Absorption spectra of reaction mixtures were measured with Unicam SP1800 and SP8000 spectrophotometers.

Termination of Living Anions of Polystyrene. In order to prepare samples of low molecular weight polymers having dibenzazepine end groups, samples of polystyrene having two living ends were quenched by reaction with BADBA in tetrahydrofuran. These experiments were kindly performed by Dr. D. H. Richards and Mrs. F. J. Burgess, ERDE, Waltham Abbey, Essex using specialized techniques previously developed for related purposes.[9] In outline the conversion of living polystyrene anion to terminal dibenzazepine units may be represented as follows:



In order to minimize side reactions the living polystyrene was first converted into the corresponding Grignard Reagent and then added dropwise to a fivefold molar excess of BADBA in THF. The resulting terminated polystyrene was then recovered by several reprecipitations into methanol. For comparison purposes a portion of the original living polystyrene was terminated and recovered by addition of methanol. This was found to have the same molecular weight as the BADBA-terminated material. The latter was clearly distinguished from the proton-terminated sample by the appearance of an IR band due to strong >C=O absorption at 1665 cm⁻¹ (film cast from $CHCl_3$).

Photosensitized Chain Extension Experiments. Appropriate solutions of purified polymers and sensitizers contained in 7 mm internal diameter Pyrex glass tubes were degassed in the usual manner before irradiation in a Rayonet merry-go-round photoreactor. The Rayonet 350 nm irradiation source was used throughout. After irradiation the glass reaction tubes were opened and the polymers were recovered by precipitation into methanol.

Molecular Weight Measurements. Number average molecular weights were estimated from measurements of solution viscosity in benzene at 30 °C with the aid of the relations:

$$[\eta] = 0.97 \times 10^{-4}\overline{M}_n^{0.74} \qquad (\text{polystyrene})^{10}$$

$$[\eta] = 0.869 \times 10^{-4}\overline{M}_n^{0.76} \qquad (\text{poly(methyl methacrylate)})^{11} \quad (6)$$

Table I
Kinetic Parameter for Photoinitiated Polymerization of Bulk Methyl Methacrylate (25 °C, λ 435.8 nm)

$10^4[Mn_2(CO)_{10}]$, mol L^{-1}	[BADBA], mol L^{-1}	Reaction time, min	$10^4\omega$, mol L^{-1} s^{-1}	$\bar{P}_n$	$k_pk_t^{-1/2}$, $mol^{-1/2}$ $L^{1/2}$ $s^{-1/2}$
6.41	0.05	10	1.49	1979	0.053
6.41	0.05	15	1.50	2015	0.053
6.41	0.05	30	1.39	2061	0.052
6.41	0.05	45	1.40	2133	0.053
9.61	0.10	15	1.48	2088	0.054
4.81	0.10	15	1.08	3054	0.056
2.40	0.10	15	0.75	3795	0.052
1.20	0.10	15	0.49	7212	0.058
					Mean 0.054

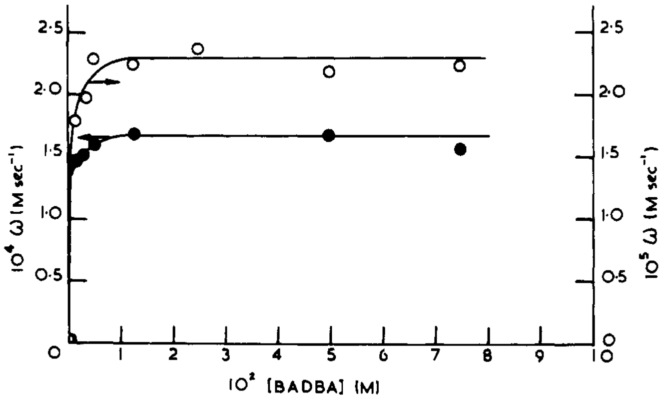


Figure 3. Polymerization of bulk methyl methacrylate (●) and bulk styrene (○) photoinitiated (λ 435.8 nm) by $Mn_2(CO)_{10}$ + BADBA. $[Mn_2(CO)_{10}] = 6.41 \times 10^{-4}$ M; reaction times 10 min (MMA) and 50 min (St); intensity constant but arbitrary. Dependence of mean rate ω on [BADBA].

Results and Discussion

Kinetic Observations. The polymerization of vinyl monomers was found to be readily photoinitiated (λ 435.8 nm) by manganese carbonyl in the presence of low concentrations of BADBA.

Methyl Methacrylate. With constant [BADBA] and incident light intensity the rate of polymerization of bulk monomer is proportional to $[Mn_2(CO)_{10}]^{1/2}$, as shown in Figure 1. The overall rate, with benzene as diluent, is first order in monomer concentration (Figure 2). These results are consistent with a simple free-radical polymerization in which initiation does not involve monomer in a rate-determining manner.

Polymers were prepared under various conditions specified in Table I and their molecular weights were determined. From corresponding values of the rate ω and the number average degree of polymerization $\bar{P}_n$ the kinetic parameter $k_pk_t^{-1/2}$ (k_p and k_t being the rate coefficients of propagation and second-order termination, respectively) was evaluated from

$$k_pk_t^{-1/2} = \frac{1}{[M]}\left\{\bar{P}_n\omega\frac{2+y}{2(1+y)}\right\}^{1/2} \tag{7}$$

in which M represents monomer and y is the ratio of combination to disproportionation in the termination reaction. We take[12] $y = 0.52$ at 25 °C. Relation 7 is valid in the absence of chain transfer and primary radical termination. The mean value of $k_pk_t^{-1/2} - 0.054$ $M^{-1/2}s^{-1/2}$ (Table I) is close to the accepted value 0.055 $M^{-1/2}s^{-1/2}$ for methyl methacrylate at 25 °C.[13] It therefore appears that chain transfer and primary termination are unimportant under the conditions described.

The dependence of the rate of polymerization on the BADBA concentration is presented in Figure 3. It has the familiar form encountered generally in free-radical polymerizations initiated by systems based on transition-metal derivatives and indicates that at concentrations exceeding 10^{-2}M, approximately (i.e., in the plateau region), BADBA does not participate in rate-determining steps in initiation.[5] Under these conditions, the rate-determining process is the photodecomposition of $Mn_2(CO)_{10}$.

We have carried out spectral observations to obtain additional information on the initiation process. Prolonged irradiation leads to the development of a band having λ_{max} 380 nm which by analogy with earlier work[5] must be attributed to $Mn(CO)_5Br$ (λ_{max} 380 nm). This derivative is formed in the radical-generating process (eq 3).

The optical density per centimeter A_t at time t during irradiation is given by the expression

$$A_t = [Mn_2(CO)_{10}]_0\{(\epsilon_1 - \beta\epsilon_2)e^{-kt} + \beta\epsilon_2\} \tag{8}$$

in which ϵ_1 and ϵ_2 are the extinction coefficients of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$, respectively, β is the number of $Mn(CO)_5Br$ molecules arising from each $Mn_2(CO)_{10}$ disappearing, and k is the first-order rate coefficient for photolysis of $Mn_2(CO)_{10}$ under the prevailing conditions. (No allowance has been made in (8) for the effect on A_t of secondary photolysis of the product $Mn(CO)_5Br$. Order-of-magnitude calculations confirm that this does not alter our conclusions.) In principle, β may have a maximum value of 2, but in view of earlier studies[5-8] a value of unity might be anticipated. We have attempted to decide between these possibilities by measurements of A_t and application of (8).

$$A_\infty = \beta\epsilon_2[Mn_2(CO)_{10}]_0 \tag{9}$$

Since (8) is equivalent to

$$\ln (A_t - A_\infty) = \ln [Mn_2(CO)_{10}]_0(\epsilon_1 - \beta\epsilon_2) - kt \tag{10}$$

Values of A_∞ (λ 380 nm) have been calculated from (9) with $\epsilon_2 = 420$ $M^{-1}cm^{-1}$ (ref 14) and $\beta = 1$ or 2. Plots of (10) are presented in Figure 4. With $\beta = 1$ the plot of ln $(A_t - A_\infty)$ vs. time is linear over the range studied (approximately 90% conversion of $Mn_2(CO)_{10}$) and corresponds to

$$k = 1.25 \times 10^{-4} \text{ s}^{-1} \tag{11}$$

On the other hand, $\beta = 2$ gives a plot which soon becomes strongly concave to the time axis. Finally, if no account is taken of the absorption of $Mn(CO)_5Br$ (i.e., $\beta = 0$) the plot is initially linear but develops convexity to the time axis, as expected. For these reasons we believe that $\beta = 1$.

It is of interest to compare the rate of consumption of manganese carbonyl with the rate of initiation of polymerization $\mathcal{I}$. The latter is readily deduced from the rate of polymerization with the aid of the conventional relation 12.

$$\omega = k_pk_t^{-1/2}[M]\mathcal{I}^{1/2} \tag{12}$$

Under the conditions of the experiments in Figure 4 with similar optical cells as reaction vessels, $\omega = 1.23 \times 10^{-4}$ M s^{-1},

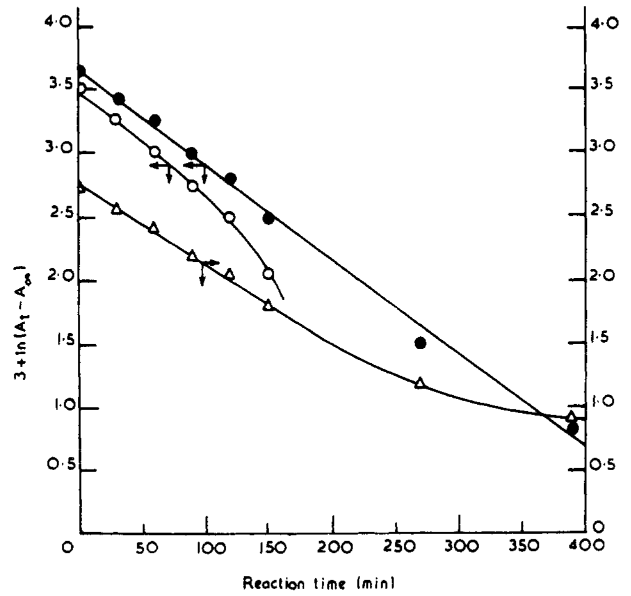


Figure 4. Polymerization of bulk methyl methacrylate photoinitiated (λ 435.8 nm) by $Mn_2(CO)_{10}$ (5.12×10^{-4} M) + BADBA (0.05 M). Plot of eq 10: (●) $\beta = 1$; (○) $\beta = 2$; (△) $\beta = 0$.

so that $\mathcal{I} = 5.87 \times 10^{-8}$ M s^{-1}. The rate of decomposition of $Mn_2(CO)_{10}$ is $k[Mn_2(CO)_{10}] = 5.94 \times 10^{-8}$ M s^{-1}. Thus each molecule of $Mn_2(CO)_{10}$ which disappears from the system gives rise to $(5.87 \times 10^{-8})/(5.94 \times 10^{-8})$, i.e., effectively one, radical. This result is clearly consistent with our assumption that the rates of radical and $Mn(CO)_5Br$ formation are equal.

The quantum yield for initiation under plateau conditions ϕ_i has been estimated by comparison of the rates of polymerization with those obtained with carbon tetrachloride as halide component. For the latter system it is known that $\phi_i = 1.0$. We find that $\phi_i = 0.6$ for $Mn_2(CO)_{10}$ + BADBA.

The conclusions we have drawn are similar to those already reached[5-8] for a wide range of photoinitiating systems based on manganese carbonyl. These have led to the view that the primary photolytic act is unsymmetrical in nature as indicated in (4). Only one type of fragment produced is considered to participate in radical formation:

$$Mn(CO)_6 + RBr \rightarrow Mn(CO)_5Br + CO + R\cdot \qquad (13)$$

Such a mechanism leads automatically to equivalence between the radical yield and the manganese carbonyl consumed. When, as in the present case, the quantum yield is less than unity in the plateau region, the second step is probably more complex; in addition to the route shown in (13), an alternative leads to the regeneration of manganese carbonyl. For details and a discussion see ref 8.

Molecular Weights of pMMA–DBA by UV Analysis of End Groups. Using *N*-acetyldibenz[*b,f*]azepine (**1a**) as a model chromophore in benzene solution (λ_{max} 287 nm, $\epsilon_{max} = 1.32 \times 10^4$ M^{-1} cm^{-1}) we may estimate the concentration of dibenzazepine end groups in relatively optically transparent pMMA samples and hence determine $\bar{M}_n$. In general, the results are in satisfactory agreement with those derived from viscosity measurements. For example, for the polymers in Table III with initial molecular weights of 55 400 and 72 200, spectrophotometrically determined values of 62 100 and 78 800 were obtained. In deducing these figures, it was assumed, in accordance with the value[11] of y quoted earlier, that the average chain carries 1.21 terminal dibenzazepine groups; further, a small correction for absorbance arising from methyl methacrylate units was applied. This result clearly supports the mechanistic proposals outlined.

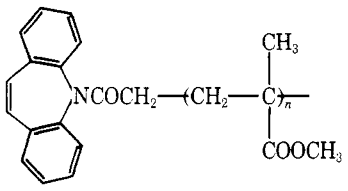
Table II
Kinetic Parameter for Photoinitiated Polymerization of Bulk Styrene (25 °C, λ 435.8 nm)[a]

$10^5\omega$, mol L^{-1} s^{-1}	$\bar{P}_n$	$k_pk_t^{-1/2}$, mol$^{-1/2}$ L$^{1/2}$ s$^{-1/2}$
2.22	840	0.0100
2.17	689	0.0098
2.37	617	0.0097
2.24	789	0.0110
2.28	641	0.0097
		Mean 0.01

[a] $[Mn_2(CO)_{10}] = 6.41 \times 10^{-4}$ mol L^{-1}; [BADBA] as in experiments of Figure 3.

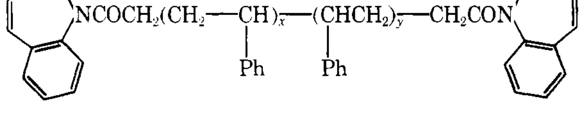
Styrene. Kinetic observations with this monomer are less extensive. Figure 3 shows the dependence of ω on [BADBA] and is similar to the corresponding curve for methyl methacrylate. Table II presents corresponding values of rates of polymerization and molecular weights for calculation of $k_pk_t^{-1/2}$. The value obtained is 0.010 M$^{-1/2}$ s$^{-1/2}$, which is satisfactorily close to published figures for styrene (cf. ref 15) in view of the uncertainties associated with the intrinsic viscosity relation. This polymerization also appears to be free from complications.

Photosensitized Chain Extension of Poly(methyl methacrylate). Since the termination reaction in methyl methacrylate polymerization occurs by disproportionation to the extent of 66%, approximately, most of the polymer molecules (~80%) prepared by $Mn_2(CO)_{10}$/BADBA initiation carry one terminal dibenzazepine unit (**3**), the remainder having two such units. After several reprecipitations into methanol the polymers were irradiated (λ 350 nm) in solution in the presence of benzil as sensitizer. Molecular weights, determined by viscosity measurements, were recorded before and after irradiation. Results are shown in Table III and indicate significant chain extension.



3 (pMMA–DBA)

Photosensitized Chain Extension of Polystyrene. Photoinitiation of styrene polymerization by means of $Mn_2(CO)_{10}$/BADBA combinations is expected to yield polystyrene molecules with a dibenzazepine unit at each end (**4**) since termination is by radical–radical combination. After several reprecipitations into methanol the polymers were irradiated (λ 350 nm) in benzene solution in the presence of benzil and benzophenone as sensitizers. Number-average molecular weights were estimated from measurements of solution viscosity, the latter being determined before and after photolysis. Results are shown in Table IV and again indicate significant chain extension.



4 (pSty–DBA)

The low molecular weight polystyrenes prepared by reac-

Table III
Benzil-Photosensitized (λ 350 nm) Chain Extension of *p*-MMA-DBA

[Polymer], g L^{-1}	[Benzil], M	Solvent	Photolysis time, h	$10^{-3}\overline{M}_n$ Initially	$10^{-3}\overline{M}_n$ After photolysis[a]	% increase in $\overline{M}_n$
100	0.2	THF	10	72.2	87.4	21
150	0.1	THF	10	72.2	77.4	7
100	0.1	THF	12.5	72.2	76.2	6
100	0.1	Benzene	40	72.2	112.6	56
100	0.1	Benzene	40	72.2	107.8	49
167	0.1	Benzene	6	55.4	70.4	27
167	0.1	CH_2Cl_2	6	55.4	61.7	11

[a] Calculated from eq 6 assuming no change in molecular weight distribution.

Table IV
Photosensitized (λ 350 nm) Chain Extension of *p*-Sty-DBA in Benzene

[Polymer], g L^{-1}	Sensitizer[a]	Photolysis time, h	$10^{-3}\overline{M}_n$ Initially	$10^{-3}\overline{M}_n$ After photolysis[d]	% increase in $\overline{M}_n$
100	Benzil	6	48.4	74.2	53.3
100	Benzophenone	6	48.4	82.9	71.3
150	Benzophenone	18	56.8	84.7	49.1
150	Benzophenone	12	56.8	87.4	53.9
150	Benzophenone	3	118.1	126.9	7.5
150	Benzophenone	6	118.1	179.7	52.2
150	Benzil	6	118.1	179.7	52.2
125[b]	Benzophenone	3	12.3[b]	69.6[b]	465.9[b]
125[b]	Benzil	4	12.3[b]	42.9[b]	248.8[b]
125[c]	Benzophenone	3	12.3[c]	12.3[c]	0[c]

[a] [Sensitizer] = 0.1 M in all cases. [b] Polystyrene sample prepared by reaction of BADBA with two-ended living polystyryl anion. [c] Reference sample prepared as in footnote *b* but terminated by reaction of living ends with methanol. [d] Calculated from eq 6 assuming no change in molecular weight distribution.

tion of BADBA with two-ended polystyryl anions were examined by GLC before and after irradiation; the measurements confirmed the occurrence of a very considerable molecular weight increase, as shown in Table IV (samples labeled *b*).

Photoinduced Gelation of *p*-Sty-DBA-*co*-DVB (DVB = divinylbenzene). As a further qualitative demonstration of photocyclo-addition involving the dibenzazepine end groups of polystyrene, the standard $Mn_2(CO)_{10}$/BADBA combination was used to initiate copolymerization of a styrene (70% v/v) divinylbenzene mixture. In preliminary experiments the gel time under standard reaction conditions (see Experimental Section) was estimated as (typically) 220 min. Soluble copolymers were then prepared by stopping reactions after periods about 5 min less than the gel time. After precipitation into methanol the *p*-Sty-DBA-*co*-DVB samples were redissolved in benzene (concentration 22.9 g L^{-1}) containing 0.1 M benzil as sensitizer and irradiated (λ 350 nm) as in the chain extension experiments. The dilute solution of copolymer was completely gelled after irradiation times of 15–30 min.

This result demonstrates conclusively the linking together of polymer molecules through terminal dibenzazepine units.

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